INVESTIGATION OF NEAR-CRITICAL STATES OF MOLYBDENUM BY METHOD OF ISENTROPIC EXPANSION [1]

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ABSTRACT

In this work release isentropes of shocked porous molybdenum were investigated. Samples with initial porosity $m=\rho_0/\rho=1,4$; 3,1 were studied to achieve near-critical entropy states of metal after shock compression. Compressed samples were expanding into helium with different initial pressure. The brightness temperature of metal and helium shock wave velocity were measured by fast multichannel pyrometer. Helium shock wave velocity value allowed to determine the final pressure (P_S) of expansion of metal and the velocity of metal expansion (W_S).

Location of peculiarities on the P_S-W_S and P_S-T_P curves of isentropes gives the location of their entrance into two-phase region. Estimation of molybdenum critical temperature and pressure were done on the basis of experimental data obtained.

KEY WORDS: critical point, isentropic expansion, molybdenum, optical pyrometry, porous sample, shock wave, spinodal.

1.INTRODUCTION

Experimental investigation of thermodynamic properties of matter in near-critical point states of liquid-vapour phase transition under isentropic expansion of samples, compressed by one-dimensional plane shock wave, have been performed in a long period of time [1]. The main part of experimental data, obtained up to present time, are the results of the measurements of the velocity of expansion of shocked metal (W_S), expanded down to the certain measured pressure (P_S) [2]. Measurements of the temperature of expanded metal are also possible by using the optical pyrometry of the process of expansion in the helium atmosphere [3-5]. The expanded states with pressures 0.1 MPa – 2 GPa are accessible, using striker with velocity of 6-7 km/s and initial helium pressure changing from 10^{-3} to 10 MPa. Using of helium as optically transparent barrier is limited by the value of velocity of expansion about 10-12 km/s with recording time being about 0.1 – 1 μs due to the beginning of ionization and loss of optical transparency of shocked helium with velocity increase. This velocity range is not enough to generate states with the critical entropy value of liquid-vapour phase transition for initially solid samples of metals with high boiling temperatures [8]. Up to now this method was used for determination of parameters of a critical point of lead and tin [3,4] only.

To investigate metals with high value of critical entropy, porous samples have been used in [2,9,10]. In this case, it is possible to reach the near-critical entropy value in a shock compression and then the near-critical states after following isentropic expansion, using the striker with common velocity value (~7 km/s). Thus, it's possible to perform pyrometric measurements of the temperatures of expanded metal. The compressed nickel powder was used as a sample in [5,6]. The technique of an estimation of critical point pressure from pyrometric measurements was similar to that used in [3,4] for solid samples. It is based on the registration of the overheating of metal by hot shocked helium in the vicinity of critical pressure. Estimation of critical point temperature have been made on the ground of the data on metal liquid spinodal below critical pressure and presentation of this line in P-T plane according some theoretical models [3,4,11].

The goal of the present study was an estimation of parameters (temperature and pressure) of the critical point of liquid - vapour transition of molybdenum from the results of experiments of isentropic expansion of shocked samples of various initial porosity.

2.MEASUREMENTS

2.1 Specimens

In the present work the flat samples of porous molybdenum (average size of particles ~ 10мкм) with densities ρ=7.2 (set 1) and ρ=3.3 g/cc (set 2) ($m = \rho/\rho_0 = 1.41$ and 3.1, were ρ - density of the sample, ρ_0 – density of solid molybdenum) were used. The sample had the shape of disk with diameter 15-20 mm and thickness 0.2 – 0.3 mm, manufactured by compression of raw molybdenum powder (samples with m=1.41), or by agglutination with alcoholic solution of butyral resin and further annealing (samples with m=3.1; mass percentage of the glue in sample was 0.05%).

2.2 Experimental setup

Experimental assembly, analogous to one, used in [5,6], is presented in Fig. 1. The sample, placed on stainless steel bottom of assembly, was shocked by the impact of steel striker with velocity 6.5 km/s up to pressures 208 GPa (for m-1.41) and with velocity 7.2 km/s – up to 109 GPa (for m=3.1) correspondingly.

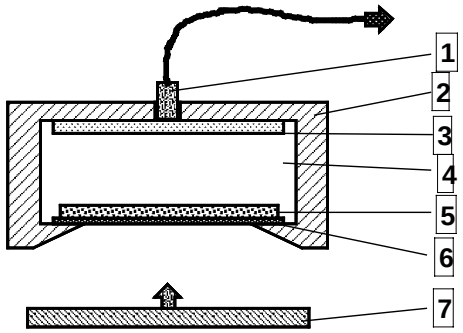

Fig.1 Experimental assembly
1. - optical fiber with aperture; 2.- pressurized case; 3.- glass window; 4. - helium under pressure; 5 - porous molybdenum sample; 6. - steel bottom of assembly; 7. - steel striker.

Optical emission was registered by multichannel optical pyrometer and recorded by fast oscilloscope “Tektronix” (TDS 5054) with time resolution 1 ns. Narrow-band filters used in the pyrometer allowed to register signals in the spectral range 700-1000 nm, with 8 nm width of spectral band. Optical emission from the experimental assembly was transmitted to the pyrometer by optical fibers.

Calculation of the brightness temperature was performed using the results of pre-shot calibration of fiber-aperture assemble with reference tungsten ribbon lamp. The black body (ε=1) emissivity of molybdenum surface was taken, the reasons of this approximation was discussed in [3]. The shock wave velocity in helium was measured by optical base length technique. Particle velocity (W_S) and pressure of expansion (P_S) were calculated, using the helium equation of state [7] (Chemical plasma model).

3.RESULTS

In this work two release isentropes with final pressures being within 0.02-2 GPa were investigated. The results of measurements of W_S - P_S dependence are presented in Fig. 2. There is a good coincidence of prediction of EOS model [8] and experimental data of W_S at high level of P_S. The increasing discrepancy of the velocities were observed under pressure diminishing below the point of isentrope entrance into two-phase region, the experimental W_S value exceeds model prediction. Such behaviour is analogous to that, observed in our previous experimental investigations [3-7] and is explained by the formation of boiling wave. The pressures of entrance of the investigated isentropes into two-phase region are 0.05±0.03 GPa (set 1) and 0.9±0.1 GPa (set 2).

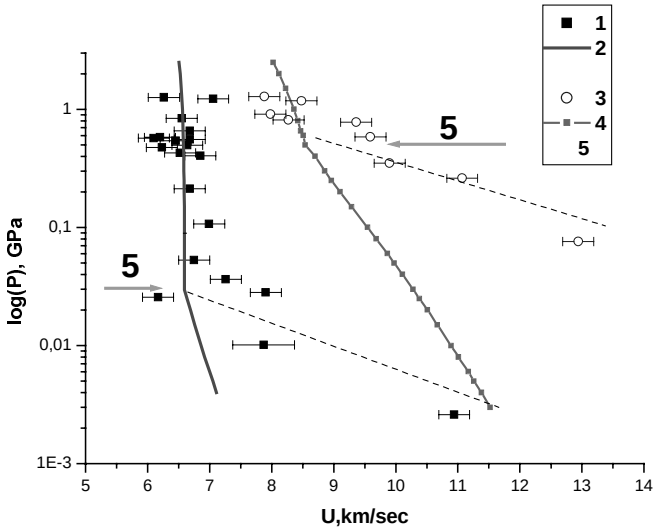

Fig.2 Pressure-particle velocity graph.
1 - experimental data for porosity m=1,41; 2 - curve-equation of state [6] calculation of release isentrope with initial porosity m=1,41; 3 - experimental data for porosity m=3,1; 4 - curve-equation of state [6] calculation of release isentrope with initial porosity m=3,1; 5 - pressure of entrance into tow-phase region.

Brightness temperature profiles from experimental snapshots for various final pressure of expansion and wavelength λ = 808 nm are shown in Fig. 3 (set 1) and Fig. 4 (set 2). A Sharp increase of the temperature up to peak value is observed in the initial moment, then, after a short interval of fast drop, very slow decrease (we can assume it a constant with 5-10% of temperature deviation) is observed. This decreasing temperature profile observed with

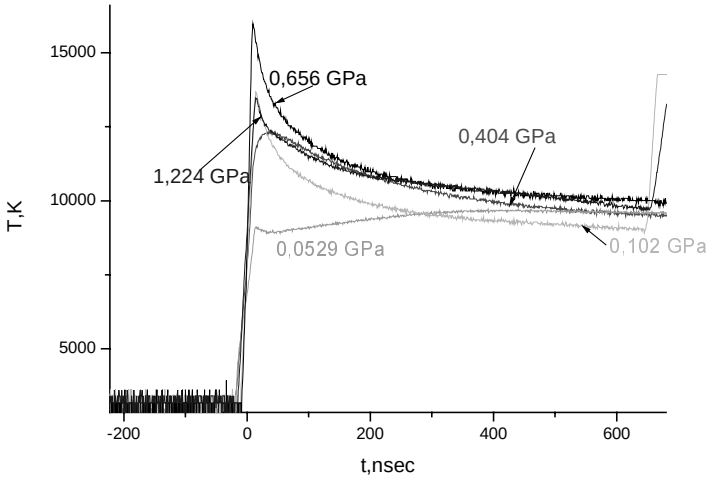

Fig.3 Typical experimental snapshots at the various finish pressures (m=1,41). Emission intensity (at λ=805nm) already converted to brightness temperature.

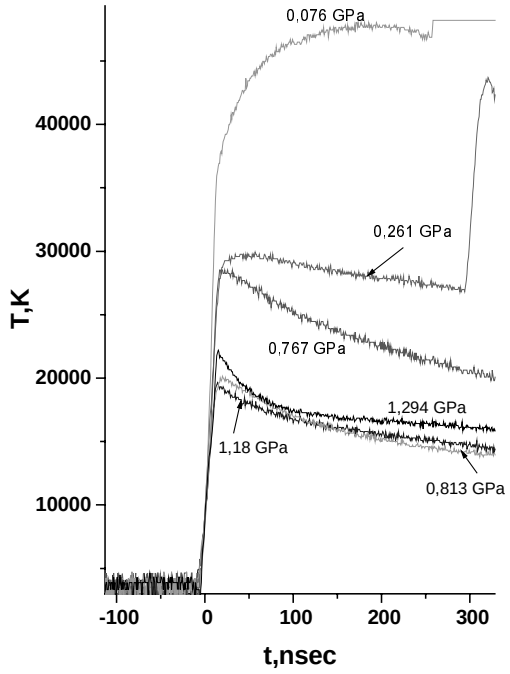

Fig.4 Typical experimental snapshots at the various finish pressures (m=3,1). Emission intensity (at λ=805nm) already converted to brightness temperature.

intervals of fast and slow decrease is due to cooling of the metal's free surface by the more cold shocked helium. Shocked helium temperature, according to its EOS model [12], was lower than measured plateau value of temperature (T_P) of the expanded molybdenum in all experiments performed. T_P versus P_S for both sets of experiments are presented in Fig. 5. Results of calculation of shocked helium temperature according

plasma model [12] from measured shock velocity for both sets of experiments are also shown in this figure.

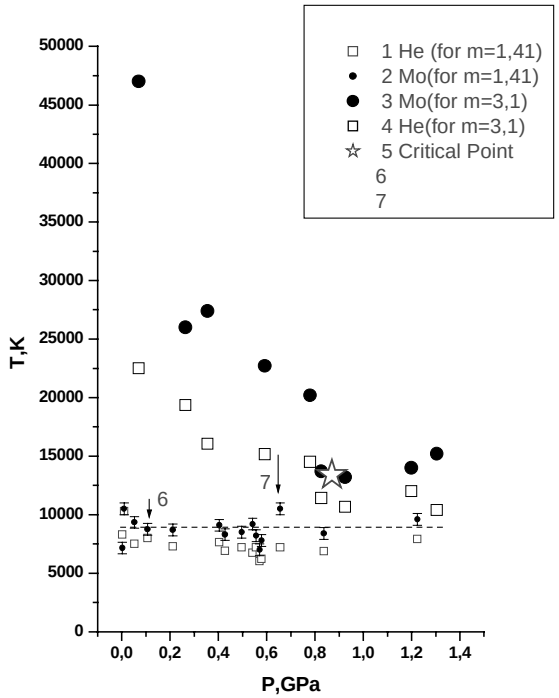

Fig.5 Pressure-temperature diagram of Mo.
1-helium temperature (m=1,41); 2-temperature of Mo on plate (m=1,41); 3- temperature of Mo on plate (m=3,1); 4 -helium temperature (m=3,1);5- critical point; 6 - the entrance into tow-phase region;7- temperature anomaly.

Calculations of states of molybdenum according model [8] indicate that expansion isentrope of Mo with initial porosity m=3.1 (set 2), shock-compressed by the impact of steel striker with velocity of 7.2 km/s is close to critical isentrope. The pressure of this isentrope entrance into two-phase region is equal to molybdenum critical point pressure (P_C) within the frameworks of experimental pressure accuracy (10%) that allows to calculate P_C from measurements of gasdynamic parameters of expansion. It should be noted, that impact of steel striker with velocity of 6.8-8.6 km/s with molybdenum sample of set 2 generates shock states which have expansion isentrope entering into two-phase region in pressure range 0.9-1 of P_C value.

The diminishing of P_S for states in the two-phase region is accompanied by the growth of T_P value (it is obviously observed for states of set 2). This abnormal growth of temperature needs further explanation.

The temperature observed in the experiment is temperature of metal-helium boundary [7]. Heat-mass transfer will lead to the diminishing of T_P with diminishing of P_S that contradicts with the results of experiments. Besides this the abnormal high peak temperatures are observed, notably higher then the temperatures of shocked molybdenum, according EOS model [8].

The metal microjets, formed on the sample free surface, can result in growth of registered temperature, but this effect cannot explain so essential growth of temperatures with pressure diminishing.

For explanation of this phenomenon the following model was suggested. In this model the observed experimental temperature value is due to behaviour of a present gas within metal pores. It was supposed adiabatic condition for metal and gas within metal pores under shock compression and during following expansion. Helium is multiple shock compressed in metal pores up to shock pressure of metal. Different compressibility of gas in pores and surrounding metal results in a different speed of pressure release within pores and metal. The process of equalization of pressure results in a perturbation of metal-gas boundary, an outburst of overheated gas from pores at a free surface of the sample, and leads to higher value of the registered temperature in comparison with metal temperature.

Calculations show, that maximal temperature of multiple-shocked gas in pore increasis linearly with decrease of initial helium pressure in acordance with experiment. In figure 6 the maximal peak temperatures registered in experiments of set 2 versus final pressure of expansion of molybdenum (curve 1, the right axis) are presented. Curve 2 (the left axis) shows the pressures of isentropic expended helium, when the temperature of gas in pores is equal to observed peak temperature. Despite of the increase of the peak temperatures with the decrease of expansion final pressure of molybdenum, the corresponding pressure of a gas in the pores decreases.

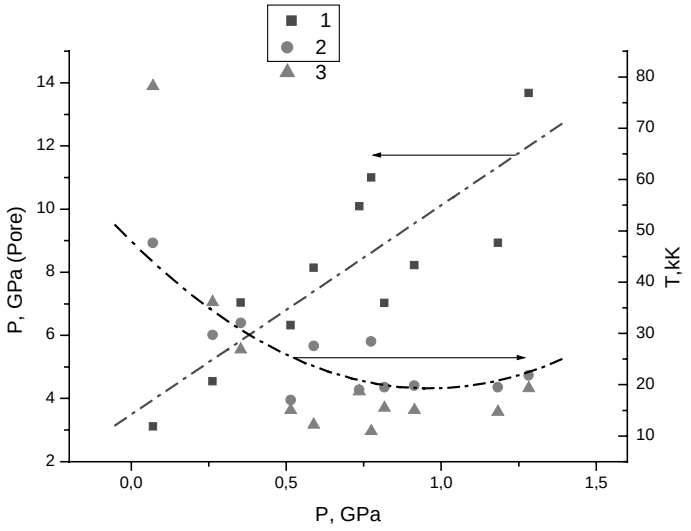

Fig.6
1 – pressure in pores versus pressure of environment at unloading; 2 – observed temperature; 3- calculated temperature of an output compressed gas in pores.

Dynamic compressibility of multiple shocked helium in pores is lower than that of surrounding compressed metal. After an entrance of a shock wave on free surface and unload wave passes through the molybdenum, the dynamic compressibility of helium decreases faster than compressibility of molybdenum (because the sound velocity in gas decreases faster, than sound velocity in metal at removal of pressure). Under certain pressure the dynamic compressibility of gas becomes lower than one of molybdenum. It

results to metal unloads faster, than gas in pores, and in some moment the pressure of gas become higher, than pressure of surrounding metal. The forces, outbursting gas from metal, arising. In fig. 6 (the curve 3, the right axis) the temperatures of helium, calculated for pressure at which the dynamic compressibility of helium and molybdenum on isentropes is equal. The good agreement of calculated and experimentally observed peak temperatures shows the validity of the supposed model.

The revealed features of the process of generation of near critical point states have not allowed to use for definition of molibdenum critical temperature approaches of [3-7]. Finally, the estimation of critical temperature was carried out by extrapolation of experimental values of temperatures for single-phase region to the pressure of an entrance into two-phase region for experimental set 2. Results of various estimations of critical pressure, temperatures [11,13-17] for molybdenum are submitted in table 1.

Table 1. Estimations of critical point parameter of molybdenum

Pc,Gpa	**Tc,K**	
0,87±0,1	13400±700	This work
0,533	13598	[16] P.R. Levashov (2000г.)
0,568	14300	[15] Seydel (1979г)
0,759	10180	[17] I.V. Lomonosov (1992)
0,692	10780	[11] M.M. Martynyuk (1983)
0,175	11330	[13] M.M. Martynyuk, P. A.Tamanda (1999)

4.CONCLUSIONS

The states of molybdenum after shock compression and the subsequent expansion of porous samples are investigated. Points of entrance of investigated isentropes into two-phase region are experimentally determined. Substantial increase of registered temperature of porous samples after shock compression and following release at the low initial helium pressure was observed, and was explained by compression of a gas in the metal pores and its thermal radiation during unloading. The estimation of pressure and temperature of a critical point of liquid - gas transition for molibdenum was performed.

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